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(54) Title: FUEL COMPOSITION FOR TWO-CYCLE ENGINES

(57) Abstract

A fuel composition for two-cycle engines comprising a major amount of fuel boiling in the gasoline range and a minor amount of a lubricant composition comprising a base oil of lubricating viscosity and an additive formulation comprising (1) a molybdenum/sulfur complex of a basic nitrogen compound, (2) a carboxylic acid amide, and (3) a succinimide.

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FUEL COMPOSITION FOR TWO-CYCLE ENGINES

BACKGROUND OF THE INVENTION

The present invention relates to a fuel composition for two-cycle internal combustion engines which comprises a major amount of fuel boiling in the gasoline range and a minor amount of a lubricant composition comprising a lubricating oil and an additive formulation containing a molybdenum/sulfur complex of a basic nitrogen compound.

Over the past several decades the use of spark-ignited two-cycle (two-stroke) internal combustion engines including rotary engines such as those of the Wankel type has steadily increased. They are presently found in power lawn mowers and other power-operated garden equipment, power chain saws, pumps, electrical generators, marine outboard engines, snowmobiles, motorcycles, and the like.

The increasing use of two-cycle engines coupled with increasing severity of the conditions in which they have operated has led to an increasing demand for oils to adequately lubricate such engines. Among the problems associated with lubrication of two-cycle engines are piston ring sticking, rusting, lubrication failure of connecting rods and main bearings and the general formation on the engine's interior surface of carbon and varnish deposits. The formation of varnish is a particularly vexatious problem since the build-up of varnish on piston and cylinder walls is believed to ultimately result in ring sticking which leads to failure of the sealing function of piston rings. Such seal failure causes loss of cylinder compression which is particularly damaging in two-cycle engines because they depend on suction to draw the new fuel charge into the

exhausted cylinder. Thus, ring sticking can lead to deterioration in engine performance, and unnecessary consumption of fuel and/or lubricant. Spark plug fouling and engine port plugging problems also occur in two-cycle engines.

A variety of compounds have been proposed as additives for fuel-lubricating oil mixtures to be used in two-cycle internal combustion engines. For example, U.S. Patent No. 4,708,809 to Davis discloses a lubricant composition for two-cycle engines comprising a major amount of an oil of lubricating viscosity and a minor amount of at least one alkyl phenol having at least one hydrocarbon-based group of at least 10 aliphatic carbon atoms. Preferably, such lubricant composition will also contain a detergent-dispersant additive selected from (i) a neutral or basic metal salt of an organic sulfur acid, phenol or carboxylic acid, (ii) a hydrocarbyl-substituted amine, (iii) an acylated, nitrogen-containing compound having a substituent of at least 10 aliphatic carbon atoms, (iv) a nitrogen-containing condensate of a phenol, aldehyde and amino compound, and (v) an ester of a substituted polycarboxylic acid.

U.S. Patent No. 4,724,091 to Davis discloses a lubricant composition for two-cycle engines comprising a major amount of an oil of lubricating viscosity and a minor amount of a mixture of at least one alkyl phenol and at least one amino phenol, each phenol having at least one hydrocarbon-based group of at least about 10 aliphatic carbon atoms. Preferably, this composition will additionally contain a detergent-dispersant additive.

U.S. Patent No. 4,740,321 to Davis et al. discloses a lubricant composition for two-cycle engines comprising a major amount of an oil of lubricating viscosity and a minor amount of at least one sulfurized alkyl phenol or metal salt thereof having at least one hydrocarbon-based group of at least 10 aliphatic carbon atoms. This lubricant composition will also preferably contain a detergent-dispersant additive.

U.S. Patent No. 4,705,643 to Nemo discloses a lubricating oil composition for two-cycle engines comprising a lubricating oil and an ashless detergent additive which is the hydrolyzed reaction product of an aliphatic branched chain carboxylic acid of 16 to 20 carbon atoms and a polyamine of at least 3 amine groups. Preferably, the ashless detergent additive is the hydrolyzed reaction product of isostearic acid and tetraethylenepentamine.

U.S. Patent No. 4,994,196 to Kagaya et al. discloses a two-cycle engine oil composition comprising a base oil and a calcium phenate detergent additive, wherein the base oil is a mixture of (a) a copolymer of an alpha-olefin with an ester of a dicarboxylic acid and (b) an ester of pentaerythritol and a fatty acid.

U.S. Patent No. 3,888,776 to Silverstein discloses a two-cycle engine lubricant which comprises a major amount of a polypropylene glycol and minor amounts of a sulfurized oxymolybdenum organophosphorodithioate, a finely divided molybdenum disulfide and a halogenated hydrocarbon detergent, such as 1,1,1-trichloroethylene, orthodichlorobenzene, perchlorinated biphenyl, and the like.

Molybdenum/sulfur complexes of basic nitrogen compounds have previously been described in the art as useful antioxidant additives for lubricant compositions finding application, for example, as crosshead diesel engine lubricants, automobile and railroad crankcase lubricants, lubricants for heavy machinery, greases for bearings, and the like.

For example, U.S. Patent No. 4,263,152 to King et al. discloses an antioxidant additive for lubricating oils which is prepared by combining an acidic molybdenum compound, a polar promoter, a basic nitrogen-containing compound and a sulfur source to form a molybdenum and sulfur-containing complex. Similar molybdenum-containing antioxidant additives are disclosed in U.S. Patent Nos. 4,285,822; 4,283,295; 4,272,387; 4,265,773; 4,261,843; 4,259,195; and 4,259,194. However, none of these patents teaches or appreciates the use of such antioxidant additives, or lubricating oils containing such additives, in admixture with fuels in two-cycle engines. Furthermore, none of these patents teaches or appreciates that such antioxidant additives would be effective deposit control agents or would reduce piston sticking when utilized in fuel-lubricating oil mixtures in two-cycle engines.

Moreover, as taught in the aforementioned U.S. Patent No. 4,708,809, the unique problems and techniques associated with the lubrication of two-cycle engines has led to the recognition by those skilled in the art of two-cycle engine lubricants as a distinct lubricant type.

Accordingly, the present invention is directed to minimizing the problems of varnish build-up and ring sticking in two-cycle engines through the provision of effective additives for fuel-lubricating oil combinations which

eliminate or reduce two-cycle engine varnish deposits and piston ring seal failure.

SUMMARY OF THE INVENTION

The present invention provides a fuel composition for two-cycle engines comprising a major amount of fuel boiling in the gasoline range and a minor amount of a lubricant composition comprising:

(A) a major amount of a base oil of lubricating viscosity, and

(B) a minor amount of an additive formulation comprising:

(1) a sulfurized molybdenum-containing composition prepared by (i) reacting an acidic molybdenum compound and a basic nitrogen compound selected from the group consisting of a succinimide, a carboxylic acid amide, a hydrocarbyl monoamine, a hydrocarbyl polyamine, a Mannich base, a phosphoramide, a thiophosphoramide, a phosphonamide, a dispersant viscosity index improver, or a mixture thereof, in the presence of a polar promoter, to form a molybdenum complex wherein from 0.01 to 2 atoms of molybdenum are present per basic nitrogen atom, and the promoter is present in the ratio of 0.01 to 50 moles of polar promoter per mole of molybdenum; and (ii) reacting the molybdenum complex with a sulfur-containing compound in an amount sufficient to provide about 1.5 to 4.0 atoms of sulfur per atom of molybdenum, to thereby form a sulfur- and molybdenum-containing composition,

(2) a carboxylic acid amide, and

(3) a succinimide.

Among other factors, the present invention is based upon the unexpected discovery that additive formulations containing a molybdenum/sulfur complex of a basic nitrogen compound, plus a carboxylic acid amide and a succinimide are surprisingly effective agents for deposit control and reduction of piston ring sticking when combined in fuel-lubricating oil mixtures in two-cycle engines.

DETAILED DESCRIPTION OF THE INVENTION

The fuel composition of the present invention will comprise a major amount of fuel boiling in the gasoline range and a minor amount of a lubricant composition comprising a base oil of lubricating viscosity and an additive formulation containing (1) a sulfurized molybdenum-containing composition, (2) a carboxylic acid amide, and (3) a succinimide.

The sulfurized molybdenum-containing composition employed in the present invention may be generally characterized as a molybdenum/sulfur complex of a basic nitrogen compound. Such molybdenum/sulfur complexes are known in the art and are described, for example, in U.S. Patent No. 4,263,152 to King et al., the disclosure of which is hereby incorporated by reference.

The precise molecular formula of the molybdenum compositions employed in this invention is not known with certainty; however, they are believed to be compounds in which molybdenum, whose valences are satisfied with atoms of

oxygen or sulfur, is either complexed by, or the salt of, one or more nitrogen atoms of the basic nitrogen containing compound used in the preparation of these compositions.

The molybdenum compounds used to prepare the molybdenum/sulfur complexes employed in this invention are acidic molybdenum compounds. By acidic is meant that the molybdenum compounds will react with a basic nitrogen compound as measured by ASTM test D-664 or D-2896 titration procedure. Typically these molybdenum compounds are hexavalent and are represented by the following compositions: molybdic acid, ammonium molybdate, sodium molybdate, potassium molybdate and other alkaline metal molybdates and other molybdenum salts such as hydrogen salts, e.g., hydrogen sodium molybdate, $MoOCl_4$, MoO_2Br_2, $Mo_2O_3Cl_6$, molybdenum trioxide or similar acidic molybdenum compounds. Preferred acidic molybdenum compounds are molybdic acid, ammonium molybdate, and alkali metal molybdates. Particularly preferred are molybdic acid and ammonium molybdate.

The basic nitrogen compound used to prepare the molybdenum/sulfur complexes must have a basic nitrogen content as measured by ASTM D-664 or D-2896. It is preferably oil-soluble. Typical of such compositions are succinimides, carboxylic acid amides, hydrocarbyl monoamines, hydrocarbon polyamines, Mannich bases, phosphoramides, thiophosphoramides, phosphonamides, dispersant viscosity index improvers, and mixtures thereof. These basic nitrogen-containing compounds are described below (keeping in mind the reservation that each must have at least one basic nitrogen). Any of the nitrogen-containing compositions may be after-treated with,

e.g., boron, using procedures well known in the art so long as the compositions continue to contain basic nitrogen. These after-treatments are particularly applicable to succinimides and Mannich base compositions.

The mono and polysuccinimides that can be used to prepare the molybdenum/sulfur complexes described herein are disclosed in numerous references and are well known in the art. Certain fundamental types of succinimides and the related materials encompassed by the term of art "succinimide" are taught in U.S. Patent Nos. 3,219,666; 3,172,892; and 3,272,746, the disclosures of which are hereby incorporated by reference. The term "succinimide" is understood in the art to include many of the amide, imide, and amidine species which may also be formed. The predominant product however is a succinimide and this term has been generally accepted as meaning the product of a reaction of an alkenyl substituted succinic acid or anhydride with a nitrogen-containing compound. Preferred succinimides, because of their commercial availability, are those succinimides prepared from a hydrocarbyl succinic anhydride, wherein the hydrocarbyl group contains from about 24 to about 350 carbon atoms, and an ethylene amine, said ethylene amines being especially characterized by ethylene diamine, diethylene triamine, triethylene tetramine, and tetraethylene pentamine. Particularly preferred are those succinimides prepared from polyisobutenyl succinic anhydride of 70 to 128 carbon atoms and tetraethylene pentamine or triethylene tetramine or mixtures thereof.

Also included within the term "succinimide" are the cooligomers of a hydrocarbyl succinic acid or anhydride and a poly secondary amine containing at least one tertiary amino nitrogen in addition to two or more secondary amino

groups. Ordinarily this composition has between 1,500 and 50,000 average molecular weight. A typical compound would be that prepared by reacting polyisobutenyl succinic anhydride and ethylene dipiperazine.

Carboxylic acid amide compositions are also suitable starting materials for preparing the molybdenum/sulfur complexes employed in this invention. Typical of such compounds are those disclosed in U.S. Patent No. 3,405,064, the disclosure of which is hereby incorporated by reference. These compositions are ordinarily prepared by reacting a carboxylic acid or anhydride or ester thereof, having at least 12 to about 350 aliphatic carbon atoms in the principal aliphatic chain and, if desired, having sufficient pendant aliphatic groups to render the molecule oil soluble with an amine or a hydrocarbyl polyamine, such as an ethylene amine, to give a mono or polycarboxylic acid amide. Preferred are those amides prepared from (1) a carboxylic acid of the formula R^2COOH, where R^2 is C_{12-20} alkyl or a mixture of this acid with a polyisobutenyl carboxylic acid in which the polyisobutenyl group contains from 72 to 128 carbon atoms and (2) an ethylene amine, especially triethylene tetramine or tetraethylene pentamine or mixtures thereof.

Another class of compounds which are useful in this invention are hydrocarbyl monoamines and hydrocarbyl polyamines, preferably of the type disclosed in U.S. Patent No. 3,574,576, the disclosure of which is hereby incorporated by reference. The hydrocarbyl group, which is preferably alkyl, or olefinic having one or two sites of unsaturation, usually contains from 9 to 350, preferably from 20 to 200 carbon atoms. Particularly preferred

hydrocarbyl polyamines are those which are derived, e.g., by reacting polyisobutenyl chloride and a polyalkylene polyamine, such as an ethylene amine, e.g., ethylene diamine, diethylene triamine, tetraethylene pentamine, 2-aminoethylpiperazine, 1,3-propylene diamine, 1,2-propylenediamine, and the like.

Another class of compounds useful for supplying basic nitrogen are the Mannich base compositions. These compositions are prepared from a phenol or C_{9-200} alkylphenol, an aldehyde, such as formaldehyde or formaldehyde precursor such as paraformaldehyde, and an amine compound. The amine may be a mono or polyamine and typical compositions are prepared from an alkylamine, such as methylamine or an ethylene amine, such as, diethylene triamine, or tetraethylene pentamine, and the like. The phenolic material may be sulfurized and preferably is dodecylphenol or a C_{80-100} alkylphenol. Typical Mannich bases which can be used in this invention are disclosed in U.S. Patent No. 4,157,309 and U.S. Patent Nos. 3,649,229; 3,368,972; and 3,539,663, the disclosures of which are hereby incorporated by reference. The last referenced patent discloses Mannich bases prepared by reacting an alkylphenol having at least 50 carbon atoms, preferably 50 to 200 carbon atoms with formaldehyde and an alkylene polyamine $HN(ANH)_nH$ where A is a saturated divalent alkyl hydrocarbon of 2 to 6 carbon atoms and n is 1-10 and where the condensation product of said alkylene polyamine may be further reacted with urea or thiourea. The utility of these Mannich bases as starting materials for preparing lubricating oil additives can often be significantly improved by treating the Mannich base using conventional techniques to introduce boron into the composition.

Another class of composition useful for preparing the molybdenum/sulfur complexes employed in this invention are the phosphoramides and phosphonamides such as those disclosed in U.S. Patent Nos. 3,909,430 and 3,968,157, the disclosures of which are hereby incorporated by reference. These compositions may be prepared by forming a phosphorus compound having at least one P-N bond. They can be prepared, for example, by reacting phosphorus oxychloride with a hydrocarbyl diol in the presence of a monoamine or by reacting phosphorus oxychloride with a difunctional secondary amine and a mono-functional amine. Thiophosphoramides can be prepared by reacting an unsaturated hydrocarbon compound containing from 2 to 450 or more carbon atoms, such as polyethylene, polyisobutylene, polypropylene, ethylene, 1-hexene, 1,3-hexadiene, isobutylene, 4-methyl-1-pentene, and the like, with phosphorus pentasulfide and a nitrogen-containing compound as defined above, particularly an alkylamine, alkyldiamine, alkylpolyamine, or an alkyleneamine, such as ethylene diamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, and the like.

Another class of nitrogen-containing compositions useful in preparing the molybdenum complexes employed in this invention includes the so-called dispersant viscosity index improvers (VI improvers). These VI improvers are commonly prepared by functionalizing a hydrocarbon polymer, especially a polymer derived from ethylene and/or propylene, optionally containing additional units derived from one or more co-monomers such as alicyclic or aliphatic olefins or diolefins. The functionalization may be carried out by a variety of processes which introduce a reactive site or sites which usually has at least one oxygen atom on the polymer. The polymer is then contacted with a

nitrogen-containing source to introduce nitrogen-containing functional groups on the polymer backbone. Commonly used nitrogen sources include any basic nitrogen compound especially those nitrogen-containing compounds and compositions described herein. Preferred nitrogen sources are alkylene amines, such as ethylene amines, alkyl amines, and Mannich bases.

Preferred basic nitrogen compounds for use in this invention are succinimides, carboxylic acid amides, and Mannich bases.

Representative sulfur sources for preparing the molybdenum complexes used in this invention are sulfur, hydrogen sulfide, sulfur monochloride, sulfur dichloride, phosphorus pentasulfide, R_2S_x where R is hydrocarbyl, preferably C_{1-40} alkyl, and x is at least 2, inorganic sulfides and polysulfides such as $(NH_4)_2S_x$, where x is at least 1, thioacetamide, thiourea, and mercaptans of the formula RSH where R is as defined above. Also useful as sulfurizing agents are traditional sulfur-containing antioxidants such as wax sulfides and polysulfides, sulfurized olefins, sulfurized carboxylic and esters and sulfurized ester-olefins, and sulfurized alkylphenols and the metal salts thereof.

The sulfurized fatty acid esters are prepared by reacting sulfur, sulfur monochloride, and/or sulfur dichloride with an unsaturated fatty ester under elevated temperatures. Typical esters include C_1-C_{20} alkyl esters of C_8-C_{24} unsaturated fatty acids, such as palmitoleic, oleic, ricinoleic, petroselinic, vaccenic, linoleic, linolenic, oleostearic, licanic, paranaric, tariric, gadoleic, arachidonic, cetoleic, etc. Particularly good results have

been obtained with mixed unsaturated fatty acid esters, such as are obtained from animal fats and vegetable oils, such as tall oil, linseed oil, olive oil, caster oil, peanut oil, rape oil, fish oil, sperm oil, and so forth.

Exemplary fatty esters include lauryl tallate, methyl oleate, ethyl oleate, lauryl oleate, cetyl oleate, cetyl linoleate, lauryl ricinoleate, oleyl linoleate, oleyl stearate, and alkyl glycerides.

Cross-sulfurized ester olefins, such as a sulfurized mixture of C_{10}-C_{25} olefins with fatty acid esters of C_{10}-C_{25} fatty acids and C_1-C_{25} alkyl or alkenyl alcohols, wherein the fatty acid and/or the alcohol is unsaturated may also be used.

Sulfurized olefins are prepared by the reaction of the C_3-C_6 olefin or a low-molecular-weight polyolefin derived therefrom with a sulfur-containing compound such as sulfur, sulfur monochloride, and/or sulfur dichloride.

Also useful are the aromatic and alkyl sulfides, such as dibenzyl sulfide, dixylyl sulfide, dicetyl sulfide, diparaffin wax sulfide and polysulfide, cracked wax-olefin sulfides and so forth. They can be prepared by treating the starting material, e.g., olefinically unsaturated compounds, with sulfur, sulfur monochloride, and sulfur dichloride. Particularly preferred are the paraffin wax thiomers described in U.S. Patent No. 2,346,156.

Sulfurized alkyl phenols and the metal salts thereof include compositions such as sulfurized dodecylphenol and the calcium salts thereof. The alkyl group ordinarily contains

from 9-300 carbon atoms. The metal salt may be preferably, a Group I or Group II salt, especially sodium, calcium, magnesium, or barium.

Preferred sulfur sources are sulfur, hydrogen sulfide, phosphorus pentasulfide, R_2S_x where R is hydrocarbyl, preferably C_1-C_{10} alkyl, and x is at least 3, mercaptans wherein R is C_1-C_{10} alkyl, inorganic sulfides and polysulfides, thioacetamide, and thiourea. Most preferred sulfur sources are sulfur, hydrogen sulfide, phosphorus pentasulfide, and inorganic sulfides and polysulfides.

The polar promoter used in the preparation of the molybdenum complexes employed in this invention is one which facilitates the interaction between the acidic molybdenum compound and the basic nitrogen compound. A wide variety of such promoters are well known to those skilled in the art. Typical promoters are 1,3-propanediol, 1,4-butane-diol, diethylene glycol, butyl cellosolve, propylene glycol, 1,4-butyleneglycol, methyl carbitol, ethanolamine, diethanolamine, N-methyl-diethanol-amine, dimethyl formamide, N-methyl acetamide, dimethyl acetamide, methanol, ethylene glycol, dimethyl sulfoxide, hexamethyl phosphoramide, tetrahydrofuran and water. Preferred are water and ethylene glycol. Particularly preferred is water.

While ordinarily the polar promoter is separately added to the reaction mixture, it may also be present, particularly in the case of water, as a component of non-anhydrous starting materials or as waters of hydration in the acidic molybdenum compound, such as $(NH_4)_6Mo_7O_{24}\cdot 4\ H_2O$. Water may also be added as ammonium hydroxide.

A method for preparing the molybdenum/sulfur complexes used in this invention is to prepare a solution of the acidic molybdenum precursor and a polar promoter with a basic nitrogen-containing compound with or without diluent. The diluent is used, if necessary, to provide a suitable viscosity for easy stirring. Typical diluents are lubricating oil and liquid compounds containing only carbon and hydrogen. If desired, ammonium hydroxide may also be added to the reaction mixture to provide a solution of ammonium molybdate. This reaction is carried out at a temperature from the melting point of the mixture to reflux temperature. It is ordinarily carried out at atmospheric pressure although higher or lower pressures may be used if desired. This reaction mixture is treated with a sulfur source as defined above at a suitable pressure and temperature for the sulfur source to react with the acidic molybdenum and basic nitrogen compounds. In some cases, removal of water from the reaction mixture may be desirable prior to completion of reaction with the sulfur source.

In the reaction mixture, the ratio of molybdenum compound to basic nitrogen compound is not critical; however, as the amount of molybdenum with respect to basic nitrogen increases, the filtration of the product becomes more difficult. Since the molybdenum component probably oligomerizes, it is advantageous to add as much molybdenum as can easily be maintained in the composition. Usually, the reaction mixture will have charged to it from 0.01 to 2.00 atoms of molybdenum per basic nitrogen atom. Preferably from 0.4 to 1.0, and most preferably from 0.4 to 0.7, atoms of molybdenum per atom of basic nitrogen is added to the reaction mixture.

The sulfur source is usually charged to the reaction mixture in such a ratio to provide 1.5 to 4.0 atoms of sulfur per atom of molybdenum. Preferably from 2.0 to 4.0 atoms of sulfur per atom of molybdenum is added, and most preferably, 2.5 to 4.0 atoms of sulfur per atom of molybdenum.

The polar promoter, which is preferably water, is ordinarily present in the ratio of 0.1 to 50 moles of promoter per mole of molybdenum. Preferably from 0.5 to 25 and most preferably 1.0 to 15 moles of the promoter is present per mole of molybdenum.

As described above, the additive formulation employed in the present invention contains (1) a sulfurized molybdenum-containing composition, (2) a carboxylic acid amide, and (3) a succinimide.

The carboxylic amide component of the presently employed additive formulation may be any of the carboxylic acid amide compounds described herein as useful in the preparation of the molybdenum/sulfur complex. Preferred carboxylic acid amide components include those amides derived from a carboxylic acid of the formula R^2COOH, wherein R^2 is C_{12}-C_{20} alkyl, and an ethylene amine, such as triethylene tetramine or tetraethylene pentamine.

Similarly, the succinimide component of the presently employed additive formulation may be any of the succinimide compounds described herein as useful in the preparation of the molybdenum/sulfur complex. Preferred succinimide components include those derived from polyisobutenyl succinic anhydride, wherein the polyisobutenyl group contains from about 50 to 250 carbon atoms, and an ethylene

amine, such as triethylene tetramine or tetraethylene pentamine.

The additive formulation employed in the present invention may additionally contain a flocculant inhibitor and/or a lubricity agent, such as a polyisobutene. If necessary, a diluent oil may also be included.

Other additives such as viscosity index improvers, antioxidants, dispersants, coupling agents, pour point depressants, extreme pressure agents, color stabilizers, rust inhibitors, anticorrosion agents, and the like, may also be present in the additive formulation.

The lubricant composition employed in the present invention comprises a major amount of a base oil of lubricating viscosity and a minor amount of the additive formulation described above.

The base oil employed may be any of a wide variety of oils of lubricating viscosity. Thus, the base oil can be a refined paraffin type base oil, a refined naphthenic base oil, or a synthetic hydrocarbon or non-hydrocarbon oil of lubricating viscosity. The base oil can also be a mixture of mineral and synthetic oils. For purposes of the present invention, the mineral lubricating oils are preferred, since they are presently in more general use in two-cycle engines.

The presently employed lubricant composition containing the additive formulation described herein can be conveniently prepared using conventional techniques by admixing the appropriate amount of each component of the additive formulation with a lubricating oil.

Generally, the amount of the molybdenum-containing additive will vary from about 0.05 to 15% by weight and preferably from about 0.2 to 10% by weight, based on the total lubricant composition, including base oil. The carboxylic acid amide component will vary from about 0.05 to 20% by weight and preferably from about 0.2 to 15% by weight. The succinimide component will vary from about 0.5 to 15% by weight and preferably from about 0.2 to 10% by weight.

The two-cycle engine fuel composition contemplated by the present invention comprises a major amount of fuel boiling in the gasoline range and minor amount of the lubricant composition disclosed herein.

For purposes of the present invention, the lubricant composition will generally be added directly to the fuel to form a mixture of lubricant and fuel which is then introduced into the two-cycle engine cylinder. Generally, the resulting fuel composition will contain from about 15 to 250 parts fuel per 1 part lubricant, and more typically about 50 to 100 parts fuel per 1 part lubricant. For some two-cycle engine applications, the lubricant may be directly injected into the combustion chamber along with the fuel or into the fuel just prior to the time the fuel enters the combustion chamber.

The fuel employed in the present fuel composition is a hydrocarbon distillate fuel boiling in the gasoline range. In such gasoline fuels, other fuel additives may also be included such as antiknock agents, e.g., methylcyclopentadienyl manganese tricarbonyl, tetramethyl or tetraethyl lead, or other dispersants or detergents such as various substituted amines, etc. Also included may be lead scavengers such as aryl halides, e.g., dichlorobenzene or

alkyl halides, e.g., ethylene dibromide. Additionally, antioxidants, metal deactivators, pour point depressants, corrosion inhibitors and demulsifiers may be present.

The following examples are presented to illustrate specific embodiments of this invention and are not to be construed in any way as limiting the scope of the invention.

EXAMPLES

Example 1

To a 5000 ml flask was added 114 grams molybdenum trioxide and 196 grams of water. Stirring was started and 1200 grams of a solution of a 45% concentrate in oil of the polyisobutenyl succinimide prepared from polyisobutenyl succinic anhydride having a number average molecular weight for the polyisobutenyl group of about 950 and tetraethylene pentamine, and 1200 grams of hydrocarbon thinner were added. The mixture was refluxed at 100°C for 3 hours. The temperature was gradually increased over approximately 1 hour to 170°C while distilling water. The temperature was maintained an additional hour after the water was removed. The temperature was lowered to 100°C-120°C and the mixture filtered and returned to the reaction vessel. To the solution was added 51 grams of sulfur. The mixture was heated to 160°C-180°C for 7 hours. The pressure was slowly reduced to about 50 mm of mercury to remove the hydrocarbon thinner. This produced 1244 grams of product containing 1.80% nitrogen, 5.63% molybdenum, and 3.57% sulfur.

Example 2

To a 5000 ml flask was added 52 grams molybdenum trioxide and 111 grams of water. Stirring was started and 1184 grams of a solution of a 45% concentrate in oil of the succinimide described in Example 1 and 1184 grams of hydrocarbon thinner were added. The mixture was refluxed at 100°C for 3 hours. The temperature was gradually increased over approximately 1 hour to 170°C while distilling water. The temperature was maintained an additional hour after the water was removed. The temperature was lowered to 100°C-120°C and the mixture filtered and returned to the reaction vessel. To the solution was added 47 grams of sulfur. The mixture was heated to 160°C-180°C for 7 hours. The pressure was slowly reduced to about 50 mm of mercury to remove the hydrocarbon thinner. This produced 1220 grams of product containing 1.94% nitrogen, 2.78% molybdenum, and 3.64% sulfur.

Example 3

To a 5000 ml flask was added 49 grams molybdenum trioxide and 105 grams of water. Stirring was started and 1133 grams of a solution of a 45% concentrate in oil of the succinimide described in Example 1 and 1133 grams of hydrocarbon thinner were added. The mixture was refluxed at 100°C for 3 hours. The temperature was gradually increased over approximately 1 hour to 170°C while distilling water. The temperature was maintained an additional hour after the water was removed. The temperature was lowered to 100°C-120°C and the mixture filtered and returned to the reaction vessel. To the solution was added 22 grams of sulfur. The mixture was heated to 160°C-180°C for 7 hours. The pressure was slowly reduced to about 50 mm of mercury to remove the hydrocarbon

thinner. This produced 1163 grams of product containing 1.83% nitrogen, 2.79% molybdenum, and 1.97% sulfur.

Example 4

To a 5000 ml flask was added 1200 grams of a polyamide prepared from a C_{18} carboxylic acid and tetraethylene pentamine and containing 6.4% nitrogen, 1200 grams hydrocarbon thinner, 42 grams molybdenum trioxide, and 90 grams water. The mixture was refluxed at 100°C for 3 hours. The temperature was gradually increased over approximately 1 hour to 170°C while distilling water. The temperature was maintained an additional hour after the water was removed. The temperature was lowered to 100°C-120°C and the mixture filtered and returned to the reaction vessel. To the solution was added 21 grams of sulfur. The mixture was heated to 160°C-180°C for 7 hours. The pressure was slowly reduced to about 50 mm of mercury to remove the hydrocarbon thinner. This produced a product containing 5.88% nitrogen, 2.29% molybdenum, and 1.63% sulfur.

Example 5

The molybdenum/sulfur complexes of Examples 1, 2 and 4 were formulated to provide lubricant compositions containing 10% of the carboxylic acid amide reaction product of isostearic acid and tetraethylene pentamine, 2% of a polyisobutenyl succinimide prepared from polyisobutenyl succinic anhydride wherein the polyisobutenyl group has a number average molecular weight of about 950 and tetraethylene pentamine, 2% of the molybdenum/sulfur complex of Examples 1, 2 and 4, respectively, 5% of a polyisobutene having a number average

molecular weight of about 950 as a lubricity agent, 0.5% of a flocculant inhibitor, 1% of a diluent oil and about 79.5% of a base oil. The base oil contains about 10% of a 150 bright stock, about 70% of a mixture of 350N and 650N neutral oils, and about 20% of a petroleum distillate solvent.

Example 6

Two-Cycle Gasoline Engine Test

This test was used to evaluate the detergency and general performance of the fuel composition of this invention in a two-cycle water-cooled outboard engine. Piston varnish, ring sticking and general engine deposits were evaluated.

The test engine used was an Outboard Marine Company Johnson Model No. J70ELEIE outboard engine, which is a 70 horsepower, water-cooled, three-cylinder, two-cycle engine.

The test procedure involved a two-hour break-in period, wherein the engine was run at 3,000 rpm for 1 hour, then at 4,000 rpm for 1 hour, using a fuel:lubricant ratio of 50:1.

The test was then conducted for 98 hours using a 50:1 fuel to lubricant ratio on a 55 minute wide-open throttle, 5 minute idle cycle. The total test time, including break-in, was 100 hours.

At the conclusion of the test, the engine was disassembled and rated. The average piston rating and average second-ring sticking rating for 3 cylinders was measured. In the rating system employed, the higher the numerical rating, the better the cleanliness performance, with 10.0

being the maximum rating. Except for the piston rings, the ratings are for cleanliness. The piston rings are rated for the degree of sticking, with a rating of 10.0 indicating a completely free piston ring.

The second-ring sticking values include a National Marine Manufacturers Association (NMMA) rating, a visual rating, and an adjusted rating, which is an average of the NMMA and visual ratings.

The reference oil employed in this test was NMMA reference oil TCW II, used as an industry standard in two-cycle engine tests to measure engine cleanliness. The TCW II reference oil is a standard mineral lubricating oil containing a commercial ashless dispersant for gasoline two-cycle engines. The reference oil is available from Citgo Petroleum Corporation, Tulsa, Oklahoma.

Engine test runs were performed with a 50:1 fuel to lubricant ratio, using lubricant compositions containing the molybdenum/sulfur complexes of Examples 1, 2 and 4, formulated as described in Example 5. The results of the engine tests are shown in Table 1.

The results shown in Table 1 demonstrate that the fuel composition of the present invention is highly effective in reducing piston deposits and piston ring sticking in two-cycle engines, and generally exceeds the performance of a fuel containing the industry standard reference oil.

TABLE 1

TWO-CYCLE ENGINE TEST RESULTS

Average Rating for 3 Cylinders							
					Second-Ring Sticking		
Additive	Piston Skirt	Crown	2-Ring Land	Under-Crown	NMMA	Visual	Adj.
TCW II Reference Oil	7.1	2.8	3.7	2.8	6.8	5.7	6.3
Example 1[(a)]	7.4	3.4	4.4	2.5	7.1	6.1	6.6
Example 4[(a)]	7.7	3.1	4.8	3.9	7.8	6.8	7.3
Example 2[(a)]	7.8	3.4	4.4	3.3	8.5	6.5	7.5

[(a)]Formulated as in Example 5.

WHAT IS CLAIMED IS:

1. A fuel composition for two-cycle engines comprising a major amount of fuel boiling in the gasoline range and a minor amount of a lubricant composition comprising:

(A) a major amount of a base oil of lubricating viscosity, and

(B) a minor amount of an additive formulation comprising:

(1) a sulfurized molybdenum-containing composition prepared by (i) reacting an acidic molybdenum compound and a basic nitrogen compound selected from the group consisting of a succinimide, a carboxylic acid amide, a hydrocarbyl monoamine, a hydrocarbyl polyamine, a Mannich base, a phosphoramide, a thiophosphoramide, a phosphonamide, a dispersant viscosity index improver, or a mixture thereof, in the presence of a polar promoter, to form a molybdenum complex wherein from 0.01 to 2 atoms of molybdenum are present per basic nitrogen atom, and the promoter is present in the ratio of 0.01 to 50 moles of polar promoter per mole of molybdenum; and (ii) reacting the molybdenum complex with a sulfur-containing compound in an amount sufficient to provide about 1.5 to 4.0 atoms of sulfur per atom of molybdenum, to thereby form a sulfur- and molybdenum-containing composition,

(2) a carboxylic acid amide, and

(3) a succinimide.

2. The fuel composition of Claim 1, wherein the sulfur source for component (1) is sulfur, hydrogen sulfide, phosphorus pentasulfide, R_2S_x where R is hydrocarbyl, and x is at least 2, inorganic sulfides or inorganic polysulfides, thioacetamide, thiourea, mercaptans of the formula RSH where R is hydrocarbyl, or a sulfur-containing antioxidant.

3. The fuel composition of Claim 2, wherein the sulfur source for component (1) is sulfur, hydrogen sulfide, phosphorus pentasulfide, R_2S_x where R is C_{1-4} hydrocarbyl, and x is at least 3, inorganic sulfides, or inorganic polysulfides, thioacetamide, thiourea or RSH where R is C_{1-40} alkyl, and the acidic molybdenum compound is molybdic acid, ammonium molybdate, or alkali metal molybdate.

4. The fuel composition of Claim 3, wherein said sulfur source is sulfur, hydrogen sulfide, RSH where R is C_{1-10} alkyl, phosphorus pentasulfide, or $(NH_4)_2S_{x'}$, where x' is at least 1, said acidic molybdenum compound is molybdic acid, or ammonium molybdate, and said basic nitrogen compound is a succinimide, carboxylic acid amide, or Mannich base.

5. The fuel composition of Claim 4, wherein said basic nitrogen compound is a C_{24-350} hydrocarbyl succinimide, carboxylic acid amide, or a Mannich base prepared from a C_{9-200} alkylphenol, formaldehyde, and an amine.

6. The fuel composition of Claim 5, wherein said basic nitrogen compound is a polyisobutenyl succinimide prepared from polyisobutenyl succinic anhydride and tetraethylene pentamine or triethylene tetramine.

7. The fuel composition of Claim 5, wherein said basic nitrogen compound is a carboxylic acid amide prepared from one or more carboxylic acids of the formula R^2COOH, or a derivative thereof which upon reaction with an amine yields a carboxylic acid amide, wherein R^2 is C_{12-350} alkyl or C_{12-350} alkenyl and a hydrocarbyl polyamine.

8. The fuel composition of Claim 7, wherein R^2 is C_{12-20} alkyl or C_{12-20} alkenyl and the hydrocarbyl polyamine is tetraethylene pentamine or triethylene tetramine.

9. The fuel composition of Claim 5, wherein said basic nitrogen compound is a Mannich base prepared from dodecylphenol, formaldehyde, and methylamine.

10. The fuel composition of Claim 5, wherein said basic nitrogen compound is a Mannich base prepared from C_{80-100} alkylphenol, formaldehyde and triethylene tetramine, tetraethylene pentamine, or mixtures thereof.

11. The fuel composition of Claim 1, wherein the polar promoter is water.

12. The fuel composition of Claim 1, wherein the carboxylic acid amide of component (2) is derived from a

carboxylic acid of the formula R^2COOH, wherein R^2 is C_{12-20} alkyl, and an ethylene amine.

13. The fuel composition of Claim 1, wherein the succinimide of component (3) is derived from polyisobutenyl succinic anhydride, wherein the polyisobutenyl group contains from about 50 to 250 carbon atoms, and an ethylene amine.

14. The fuel composition of Claim 1, wherein the lubricant composition contains about 0.05 to 15% by weight of the molybdenum-containing composition of component (1), about 0.05 to 20% by weight of the carboxylic acid amide of component (2), and about 0.05 to 15% by weight of the succinimide of component (3).

15. The fuel composition of Claim 1, wherein the molybdenum complex is reacted with the sulfur-containing compound in an amount sufficient to provide about 2.0 to 4.0 atoms of sulfur per atom of molybdenum.

16. The fuel composition of Claim 15, wherein the molybdenum complex is reacted with the sulfur-containing compound in an amount sufficient to provide about 2.5 to 4.0 atoms of sulfur per atom of molybdenum.

17. The fuel composition of Claim 1, wherein the additive formulation further contains a flocculant inhibitor.

18. The fuel composition of Claim 17, wherein the additive formulation further contains a lubricity agent.

19. A method for reducing engine deposits and piston ring sticking in a two-cycle engine which comprises operating the two-cycle engine with a fuel composition comprising a major amount of fuel boiling in the gasoline range and a minor amount of a lubricant composition comprising:

(A) a major amount of a base oil of lubricating viscosity, and

(B) a minor amount effective to reduce engine deposits and piston ring sticking of an additive formulation comprising:

(1) a sulfurized molybdenum-containing composition prepared by (i) reacting an acidic molybdenum compound and a basic nitrogen compound selected from the group consisting of a succinimide, a carboxylic acid amide, a hydrocarbyl monoamine, a hydrocarbyl polyamine, a Mannich base, a phosphoramide, a thiophosphoramide, a phosphonamide, a dispersant viscosity index improver, or a mixture thereof, in the presence of a polar promoter, to form a molybdenum complex wherein from 0.01 to 2 atoms of molybdenum are present per basic nitrogen atom, and the promoter is present in the ratio of 0.01 to 50 moles of polar promoter per mole of molybdenum; and (ii) reacting the molybdenum complex with a sulfur-containing compound in an amount sufficient to provide about 1.5 to 4.0 atoms of sulfur per atom of molybdenum, to thereby

form a sulfur- and molybdenum-containing composition;

(2) a carboxylic acid amide; and

(3) a succinimide.

20. The method of Claim 19 wherein the sulfur source for component (1) is sulfur, hydrogen sulfide, phosphorus pentasulfide, R_2S_x where R is hydrocarbyl, and x is at least 2, inorganic sulfides or inorganic polysulfides, thioacetamide, thiourea, mercaptans of the formula RSH where R is hydrocarbyl, or a sulfur-containing antioxidant.

21. The method of Claim 20 wherein the sulfur source for component (1) is sulfur, hydrogen sulfide, phosphorus pentasulfide, R_2S_x where R is C_{1-4} hydrocarbyl, and x is at least 3, inorganic sulfides, or inorganic polysulfides, thioacetamide, thiourea or RSH where R is C_{1-40} alkyl, and the acidic molybdenum compound is molybdic acid, ammonium molybdate, or alkali metal molybdate.

22. The method of Claim 21 wherein said sulfur source is sulfur, hydrogen sulfide, RSH where R is C_{1-10} alkyl, phosphorus pentasulfide, or $(NH_4)_2S_{x'}$, where x' is at least 1, said acidic molybdenum compound is molybdic acid, or ammonium molybdate, and said basic nitrogen compound is a succinimide, carboxylic acid amide, or Mannich base.

23. The method of Claim 22 wherein said basic nitrogen compound is a C_{24-350} hydrocarbyl succinimide, carboxylic acid amide, or a Mannich base prepared from a C_{9-200} alkylphenol, formaldehyde, and an amine.

24. The method of Claim 23 wherein said basic nitrogen compound is a polyisobutenyl succinimide prepared from polyisobutenyl succinic anhydride and tetraethylene pentamine or triethylene tetramine.

25. The method of Claim 23 wherein said basic nitrogen compound is a carboxylic acid amide prepared from one or more carboxylic acids of the formula R^2COOH, or a derivative thereof which upon reaction with an amine yields a carboxylic acid amide, wherein R^2 is C_{12-350} alkyl or C_{12-350} alkenyl and a hydrocarbyl polyamine.

26. The method of Claim 25 wherein R^2 is C_{12-20} alkyl or C_{12-20} alkenyl and the hydrocarbyl polyamine is tetraethylene pentamine or triethylene tetramine.

27. The method of Claim 23 wherein said basic nitrogen compound is a Mannich base prepared from dodecylphenol, formaldehyde, and methylamine.

28. The method of Claim 23 wherein said basic nitrogen compound is a Mannich base prepared from C_{80-100} alkylphenol, formaldehyde and triethylene tetramine, tetraethylene pentamine, or mixtures thereof.

29. The method of Claim 19 wherein the polar promoter is water.

30. The method of Claim 19 wherein the carboxylic acid amide of component (2) is derived from a carboxylic acid of the formula R^2COOH, wherein R^2 is C_{12-20} alkyl, and an ethylene amine.

31. The method of Claim 19 wherein the succinimide of component (3) is derived from polyisobutenyl succinic anhydride, wherein the polyisobutenyl group contains from about 50 to 250 carbon atoms, and an ethylene amine.

32. The method of Claim 19 wherein the lubricant composition contains about 0.05 to 15% by weight of the molybdenum-containing composition of component (1), about 0.05 to 20% by weight of the carboxylic acid amide of component (2), and about 0.05 to 15% by weight of the succinimide of component (3).

33. The method of Claim 19 wherein the molybdenum complex is reacted with the sulfur-containing compound in an amount sufficient to provide about 2.0 to 4.0 atoms of sulfur per atom of molybdenum.

34. The method of Claim 33 wherein the molybdenum complex is reacted with the sulfur-containing compound in an amount sufficient to provide about 2.5 to 4.0 atoms of sulfur per atom of molybdenum.

35. The method of Claim 19 wherein the additive formulation further contains a flocculant inhibitor.

36. The method of Claim 35 wherein the additive formulation further contains a lubricity agent.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/08471

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C10M 159/18, 133/16, 149/00
US CL :252/42.7, 46.4, 51.5A
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/42.7, 46.4, 51.5A, 44/367, 330,331

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,263,152 (King et al) 21 April 1981, see col. 2, lines 10 et seq. and col. 7, lines 5-47.	1-36
Y	US, A, 3,405,064 (Miller) 08 October 1968, see col. 1, lines 19-40 and lines 55 et seq.	1-36
Y	US, A, 3,219,666 (Norman et al) 23 November 1965, see entire document.	1-36
A	US, A, 4,266,945 (Karn) 12 May 1981, see entire document.	1-36
A	US, A, 4,164,473 (Coupland et al) 14 August 1979, see entire document.	1-36

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

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Date of the actual completion of the international search	Date of mailing of the international search report
19 NOVEMBER 1993	05 JAN 1994

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